

Control of the diameter and chiral angle distributions during production of single-wall carbon nanotubes

Abstract

Many applications of single wall carbon nanotubes (SWCNT), especially in microelectronics, will benefit from use of certain (n,m) nanotube types (metallic, small gap semiconductor, etc.). However, as produced SWCNT samples are polydispersed, with many (n,m) types present and typical ~1:2 metal/semiconductor ratio. It has been recognized that production of SWCNTs with narrow “tube type populations” is beneficial for their use in applications, as well as for the subsequent sorting efforts.

In the present work, SWCNTs were produced by a pulsed laser vaporization (PLV) technique. The nanotube type populations were studied with respect to the production temperature with two catalyst compositions: Co/Ni and Rh/Pd. The nanotube type populations were measured via photoluminescence, UV-Vis-NIR absorption and Raman spectroscopy.

It was found that in the case of Co/Ni catalyst, decreased production temperature leads to smaller average diameter, exceptionally narrow diameter distribution, and strong preference toward (8,7) nanotubes. The other nanotubes present are distributed evenly in the 7-30° chiral angle range. In the case of Rh/Pd catalyst, a decrease in the temperature leads to a small decrease in the average diameter, with the chiral angle distribution skewed towards 30° and a preference toward (7,6), (8,6) and (8,7) nanotubes. However, the diameter distribution remains rather broad. These results demonstrate that PLV production technique can provide at least partial control over the nanotube (n,m) populations. In addition, these results have implications for the understanding the nanotube nucleation mechanism in the laser oven.

Control of the diameter and chiral angle distributions during production of single-wall carbon nanotubes

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Abstract

Pulsed laser vaporization synthesis of single-wall carbon nanotubes on Co/Ni and Rh/Pd catalysts was explored with respect to variations in the production temperature. The nanotube type populations were determined via photoluminescence, UV-Vis-NIR absorption and Raman spectroscopy. It was found that lowered production temperature leads to smaller nanotube diameters and exceptionally narrow (n,m) type distributions, with marked preference towards large chiral angles for both catalysts.

Interestingly, larger nanotube diameters tend to be associated with larger chiral angles. These results demonstrate that PLV production technique can provide at least partial control over the nanotube (n,m) populations. In addition, these results have implications for the understanding the nanotube nucleation mechanism in the laser oven. SWCNT synthesized at lower temperatures appear quite attractive as a starting material for nanotube type separation experiments.

- The production of SWCNTs with narrow “tube type populations” might be beneficial for the subsequent separation efforts.
 - However, there are very few reports on production of nanotube samples enriched in certain nanotube types.
- Some known examples:
 - Low temperature CoMoCat SWCNTs, that are naturally enriched in (6,5), (7,5) and (7,6) types. G. Lolli, L. Zhang, L. Balzano, N. Sakulchaicharoen, Y. Tan, and D. E. Resasco, *J. Phys. Chem. B* 110, 2108 (2006).
 - SWCNTs produced by alcohol CVD technique at lower temperatures are similarly enriched in the (6,5), (7,5) and (7,6) types. Y. Miyauchi, S. Chiashi, Y. Murakami, Y. Hayashida, and S. Maruyama, *Chem. Phys. Lett.* 387, 198 (2004).
 - SWCNT samples enriched in (7,6) type were also produced by pulsed laser vaporization (PLV) technique on Rh/Pd catalyst. S. Suzuki, N. Asai, H. Kataura, and Y. Achiba, *Eur. Phys. J. D* 43, 143 (2007).
- It seems SWCNT synthesis at lowered temperatures leads to enrichment in certain (n,m) types. Interestingly, *semiconducting* nanotubes with chiral angles skewed to arm-chair structures are reported in all these works. Presence of metallic nanotubes has not been analyzed.
 - *Are these samples enriched in arm-chair metallic tubes as well?*

•So, it was decided to explore the effect production temperature has on nanotube (n,m) populations in our pulsed laser vaporization (PLV) setup.

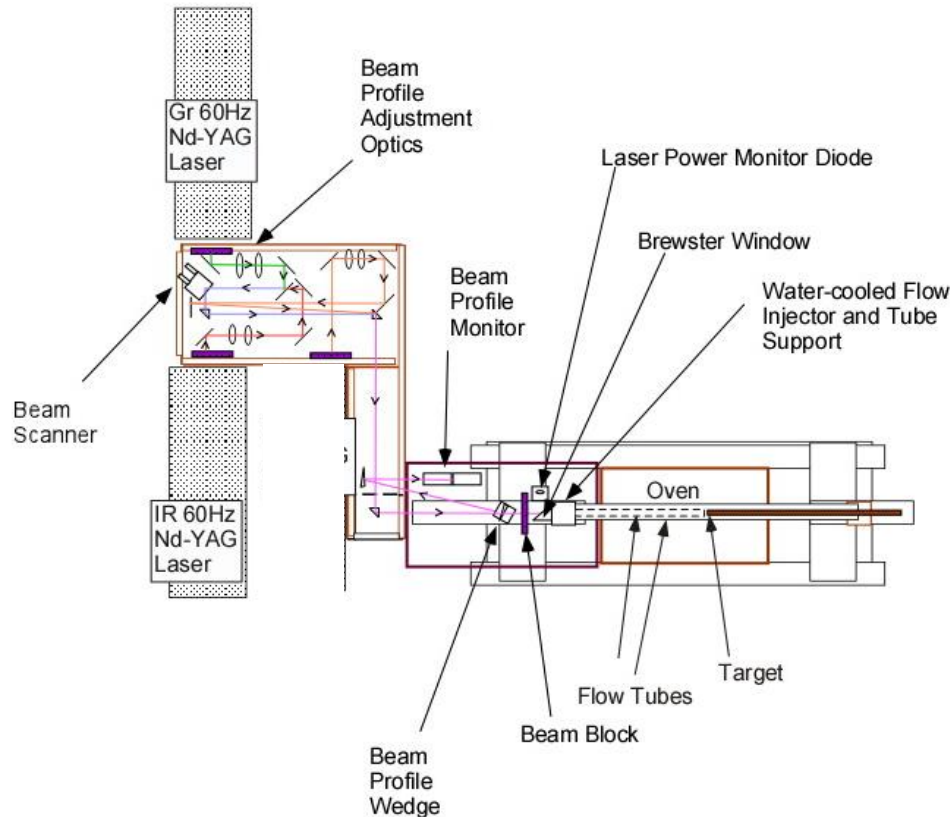
•Early findings:

•Co/Ni catalyst barely produces any SWCNT below 900 °C

•Rh/Pd catalyst barely produces any SWCNT at 500 Torr pressure -> runs were done at 750 Torr pressure

- Co/Ni catalyst (1 atomic % each)
- Argon buffer gas
- 500 Torr pressure
- 100 sccm flow rate
- Green/IR laser combination with 50 ns pulse delay
- 1.6 J/cm² energy density (each)
- 60 Hz repetition rate
- Temperatures: 900°C, 1000°C, 1100°C (below standard 1200 °C)**

- Rh/Pd catalyst (1 atomic % each)
- Argon buffer gas
- 750 Torr pressure
- 100 sccm flow rate
- Green/IR laser combination with 50 ns pulse delay
- 1.6 J/cm² energy density (each)
- 60 Hz repetition rate
- Temperatures: 1100°C, 1150°C, 1200°C (at and below maximum allowed 1200 °C)**

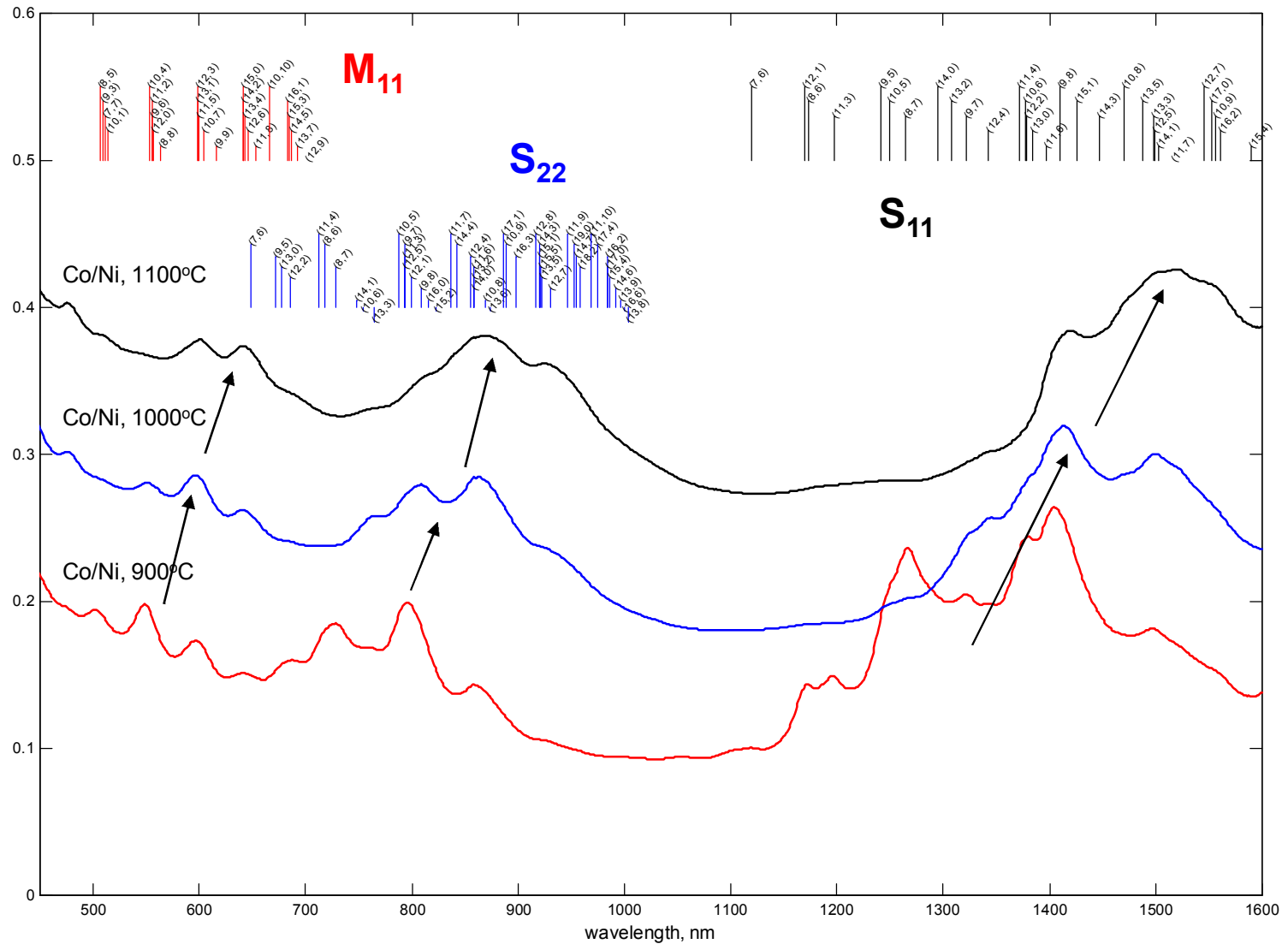


(n,m) analysis:

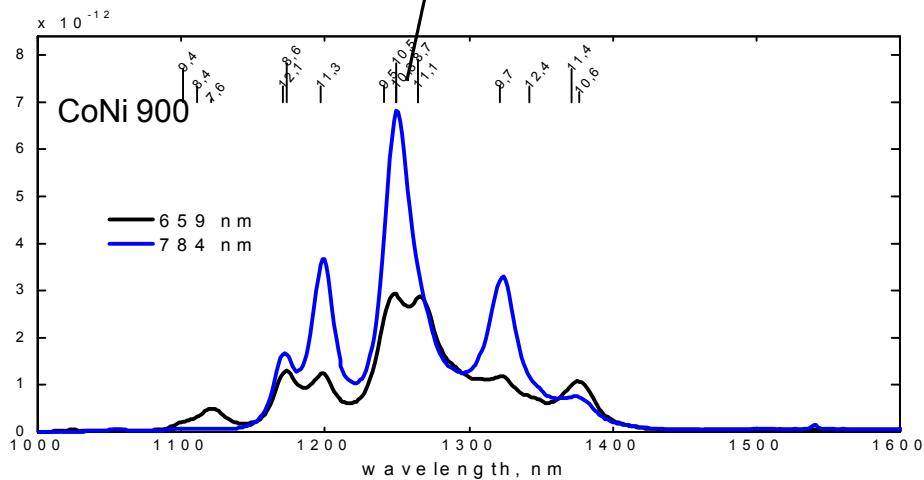
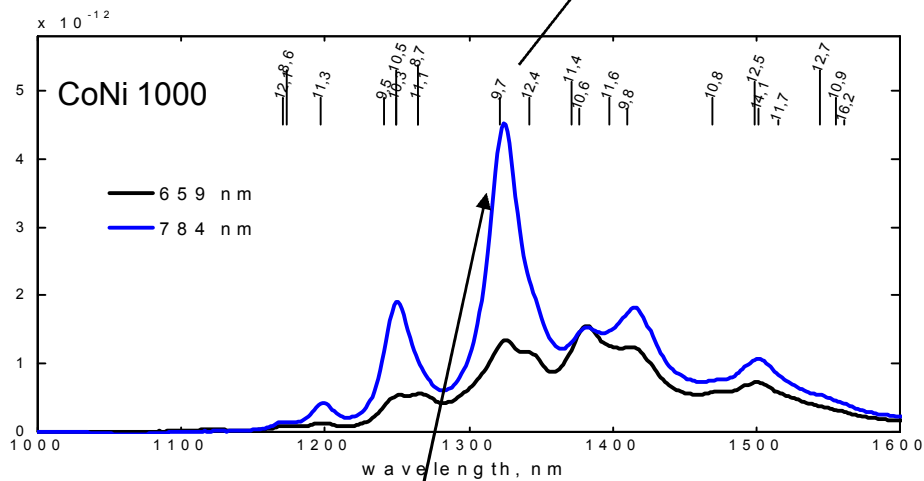
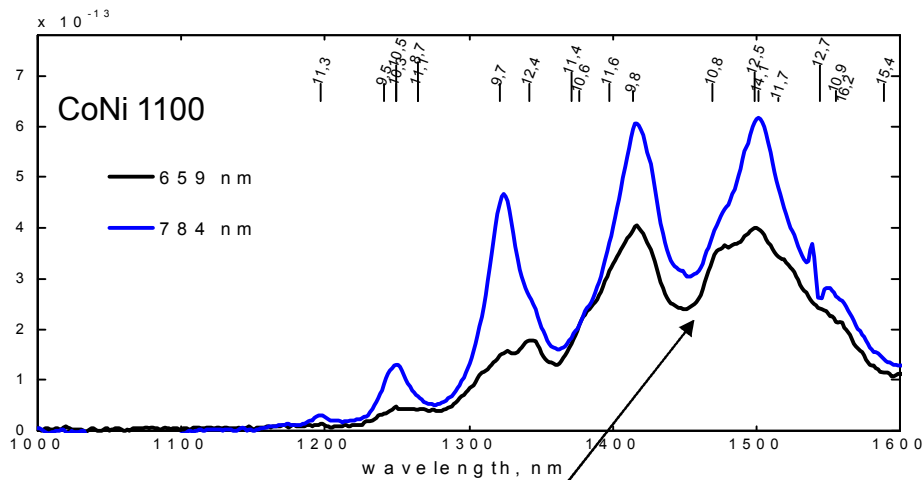
- Samples dispersed in H₂O / SDBS 1.5 wt.% by ultrasonication, and centrifuged at 74,000g for 2 hrs.
- Emission spectroscopy: no access to Fluorolog-type emission spectrometer. Used Nanospectralyzer™ that excites emission with two lasers, 659 or 784 nm wavelength (Applied Nanofluorescence LLC)
- Absorption spectroscopy: Perkin Elmer Lambda 900
- Raman spectroscopy: Renishaw InVia Raman microscope, three excitation wavelengths: 514, 633 and 785 nm. Raman spectra acquired on dry samples.
- Strategy for (n,m) analysis:
 1. For each semiconducting nanotube, its presence is checked in the emission, absorption and Raman spectra, taking into account how far it is from the resonance with excitation lasers in case of emission and Raman spectra.
 2. Then metallic nanotubes are identified according to the remaining spectral features on absorption and Raman spectra, taking into account the possibility of overlapping with semiconducting nanotubes.
- Attempts to fit absorption and PL spectra with a number of Lorentzian lines corresponding to nanotube types present in the samples turned out to be inconclusive. The precise transition energies are sensitive to the environment, and small change in the transition energies of two closely overlapping peaks led to large variations in the respective peak intensities. Apart from that, the fitting of the absorption spectra was found to be sensitive to the variations in the background subtraction
- The relationships between nanotube concentration and intensity of its spectral features are not known accurately, and are known to vary quite a bit among nanotube types.
- Therefore, nanotube populations were simply expressed as “major” nanotube types with very strong spectral features and “minor” nanotube types with weaker but definitely detectable spectral features.

Absorption spectra of Co/Ni samples.

Temperature increase -> absorption features shift towards longer wavelength -> larger diameter nanotubes



Emission spectra of Co/Ni samples

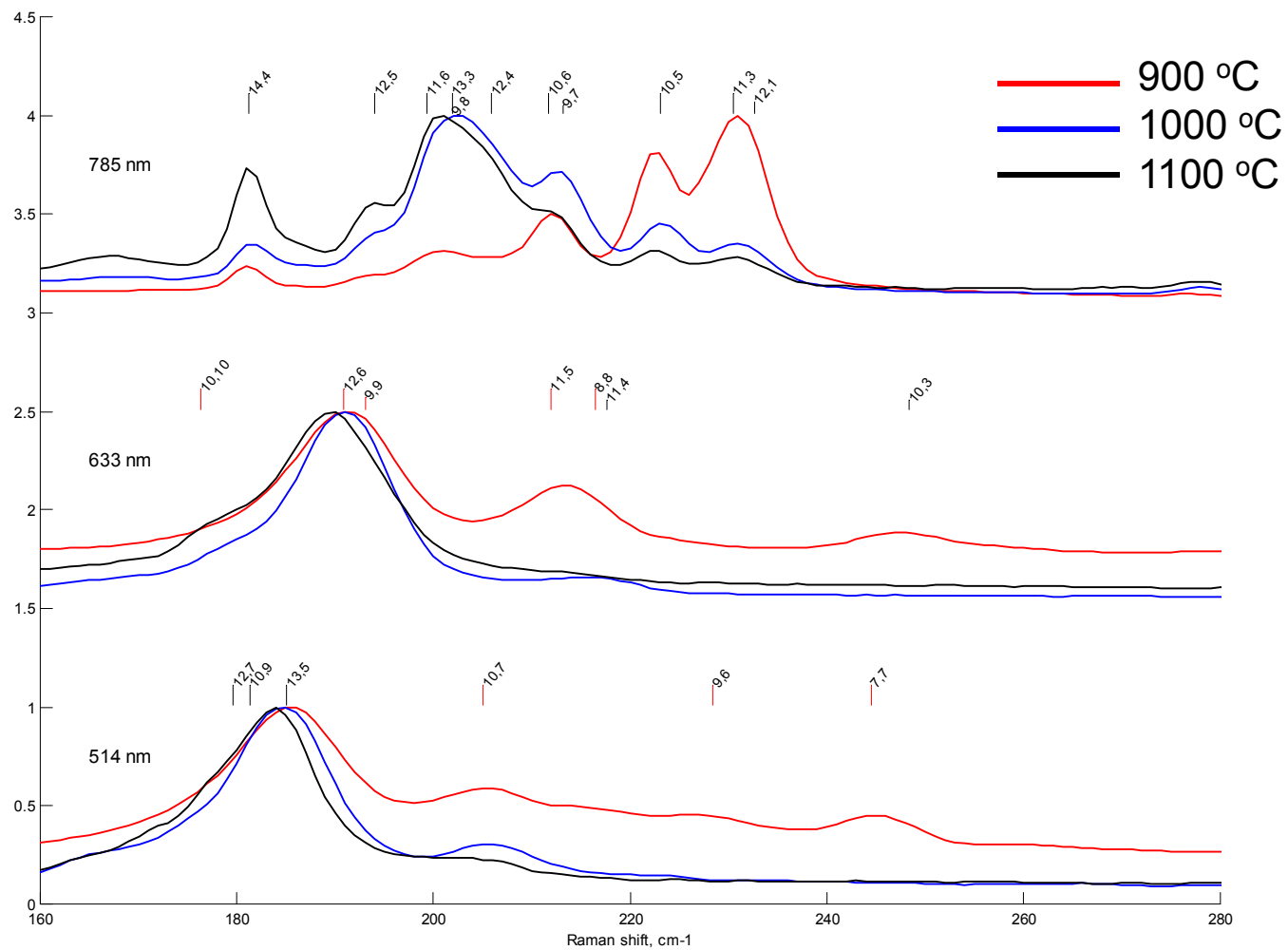


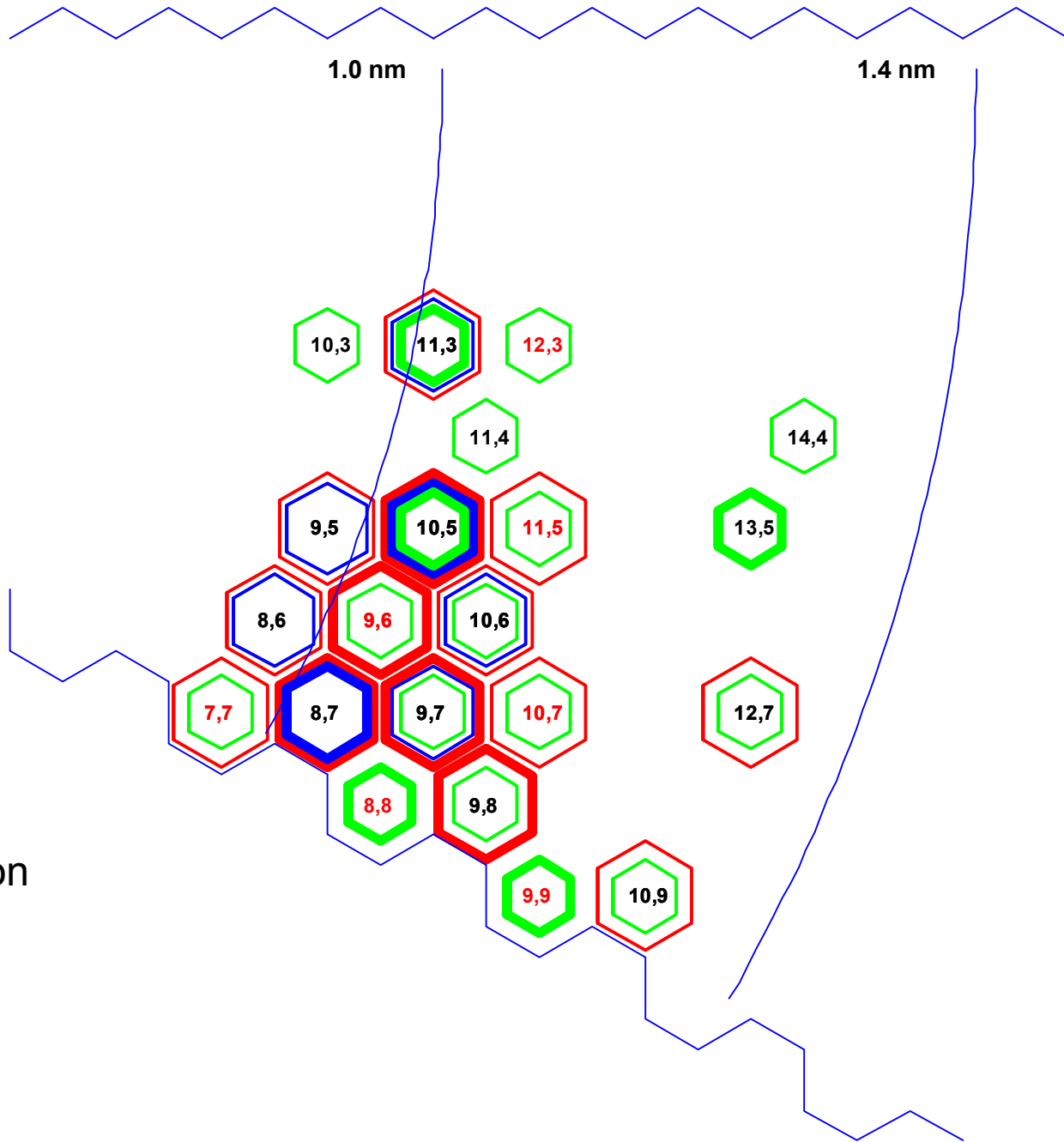
Temperature increase -> emission features shift towards longer wavelength
-> larger diameter nanotubes




At 1000 °C and above, some emission is out of the detector range.

Emission wavelength range is rather narrow for 900°C sample

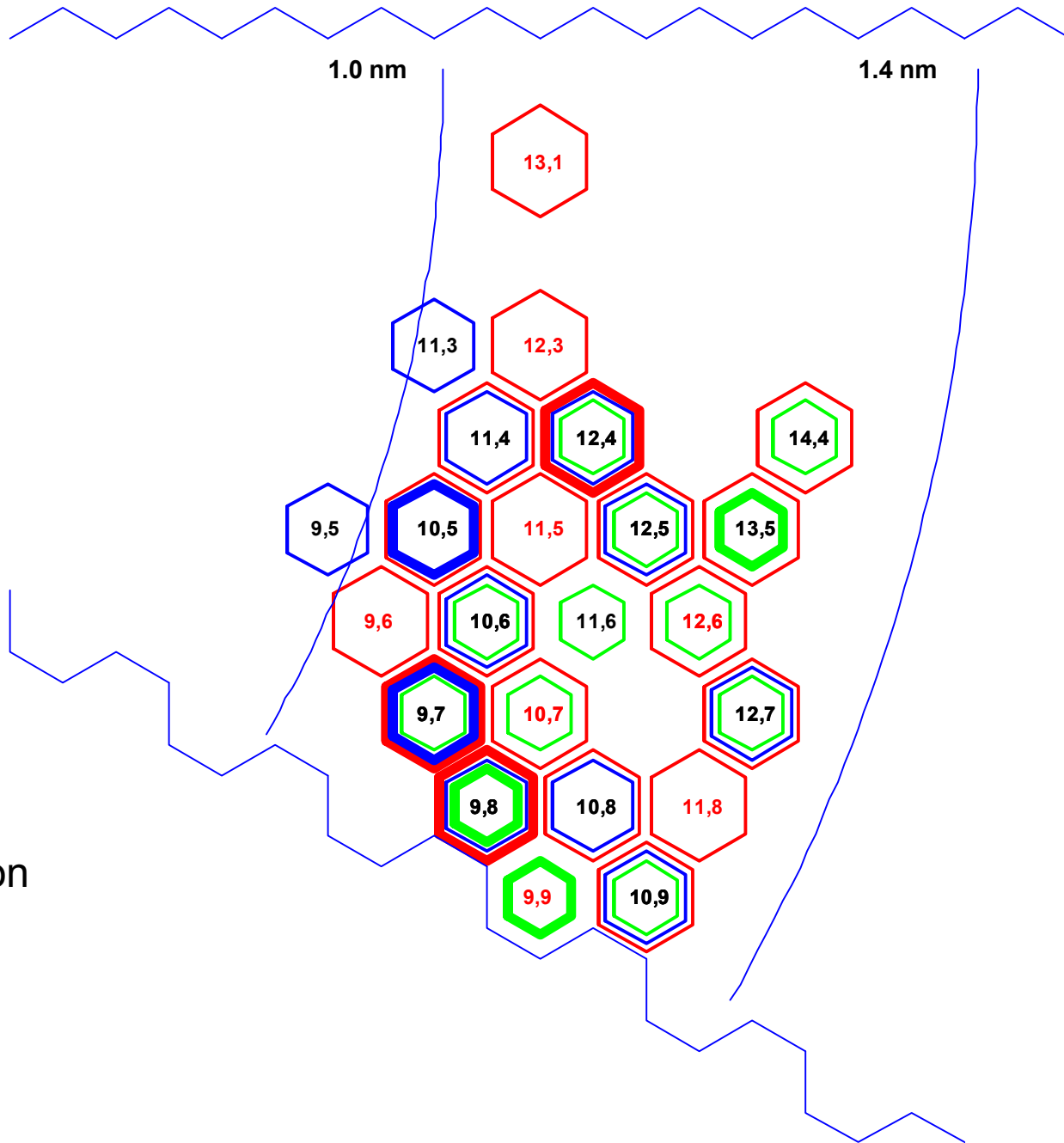
Raman RBM spectra of Co/Ni samples:



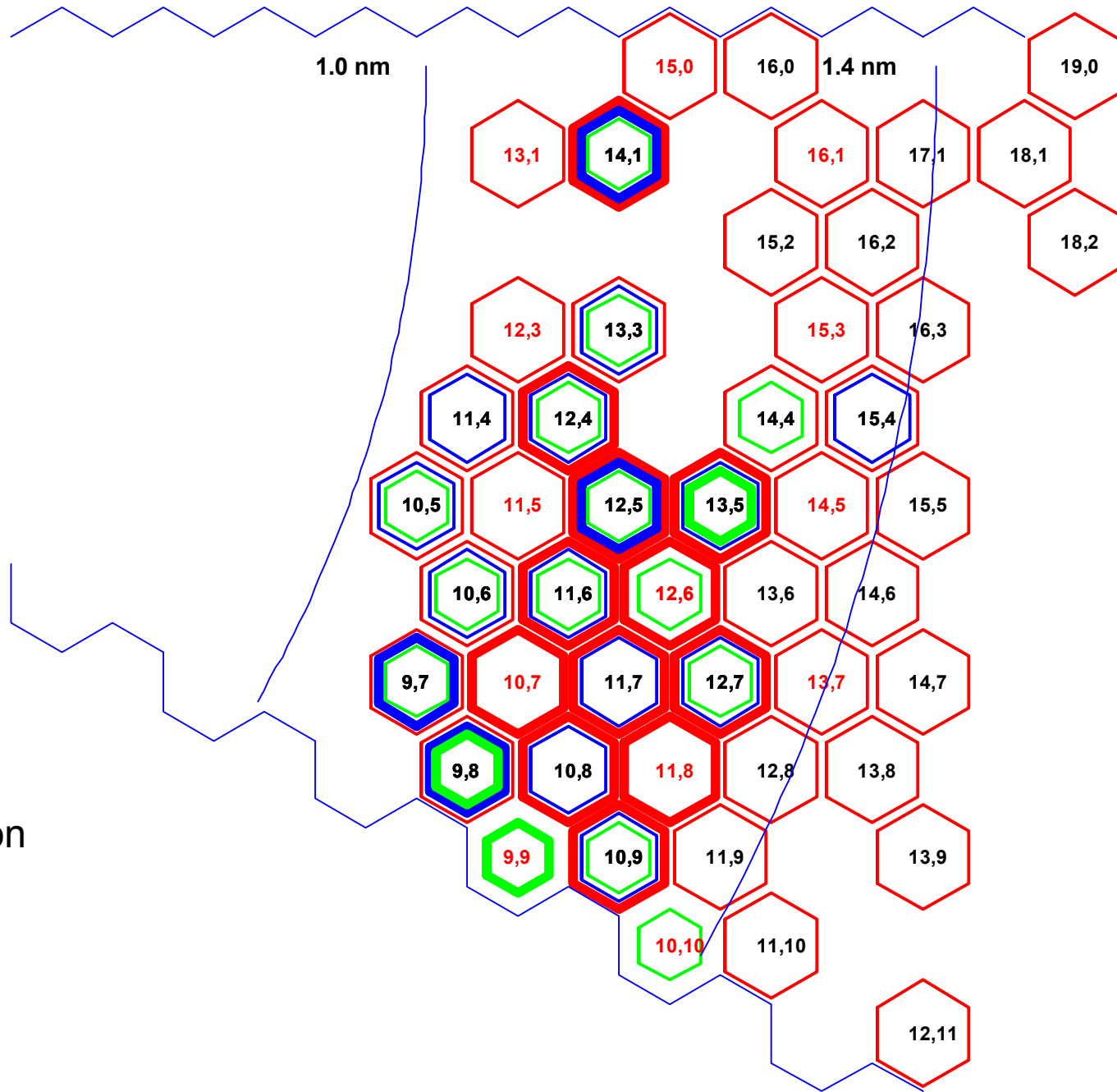


-  Absorption
-  Emission
-  Raman

CoNi900



CoNi1000



CoNi1100

Observations:

As the temperature is increased:

Average diameter increases

The width of diameter distribution increases

The chiral angle distribution is close to 30° at 900°C and shifts to smaller angles at higher temperatures

The type distribution is rather narrow at 900°C :

Metallic nanotubes:

-strongest: (7,7), -armchair metals: (8,8) and (9,9), -chiral metals: (9,6), (10,5), (11,3) } all have very close diameters in 1.00 – 1.05 nm range.

Semiconductors: -strongest: (8,7), -close to arm-chair: (9,7), (9,8),

-less dominant: (8,6), (9,7), (10,6), (10,5), (11,4), (11,3), (12,4), (12,2) and (13,2).

Another very interesting observation:

- For 900°C sample, absorption peak at $\sim 505\text{ nm}$ is an overlap of (8,5) (9,3) (10,1) and (7,7) tubes. All have very close M_{11} energies close to Raman 514 nm excitation. However, all but (7,7) are absent on Raman RBM spectrum, i.e. this absorption peak belongs exclusively to (7,7) arm-chair nanotube.

- On the other hand, while (8,8) and (9,9) nanotubes are easily identified on Raman 633 nm excitation spectrum, their transition energies are far enough from the absorption peaks 550 and 600 nm (that are much better identified with (9,6) and (10,7) tubes also present on Raman spectra).

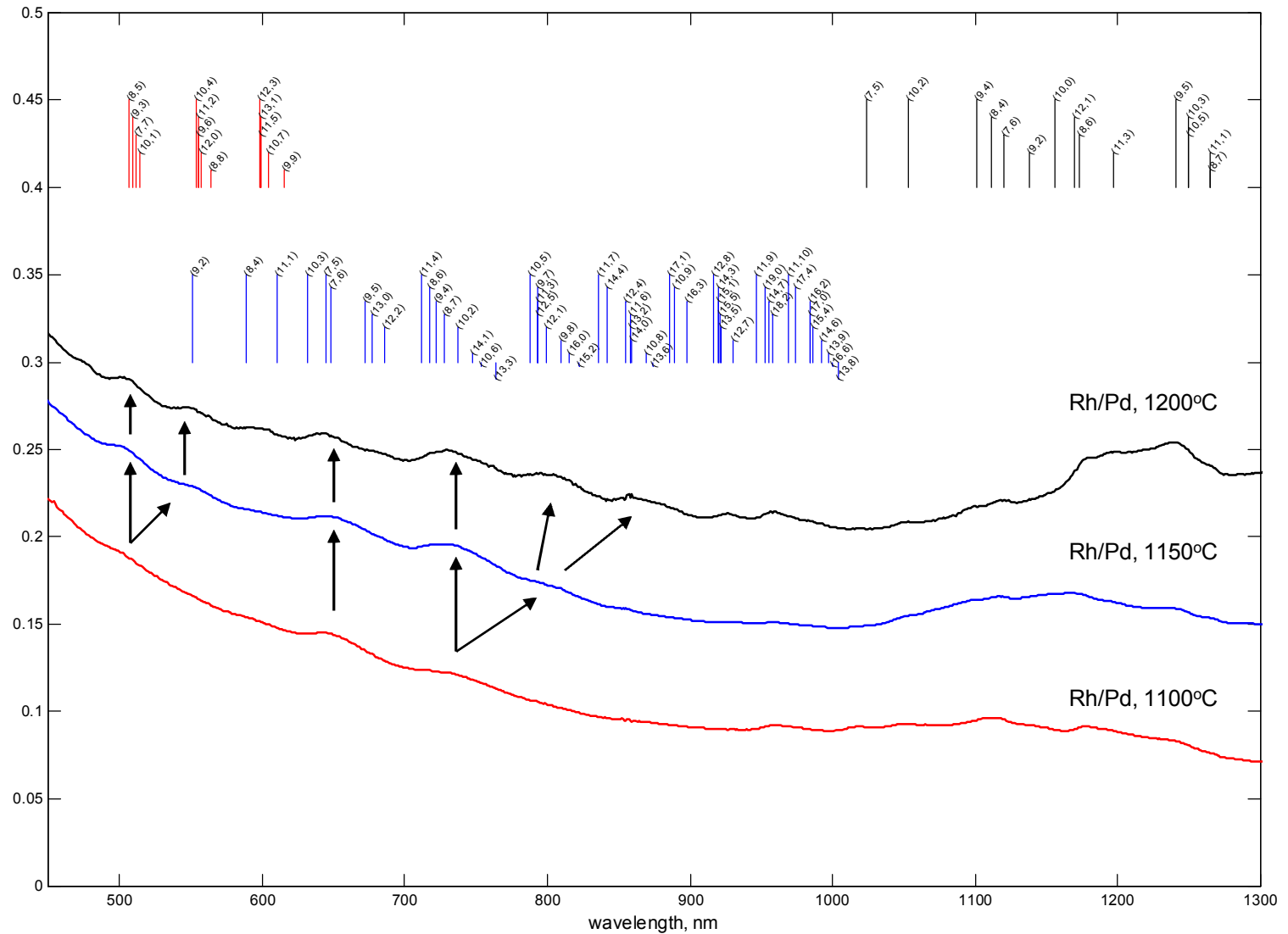
- We can conclude that optical absorption by (8,8) and (9,9) armchair tubes is very small if nonexistent, while optical absorption by (7,7) armchair tube is substantial. Small optical absorption for armchair nanotubes has been predicted theoretically in [1] based on symmetry considerations. Therefore, our observation for (7,7) tube is strange.

For all Co/Ni samples, and especially 900°C sample, larger diameter nanotubes are associated with larger chiral angles.

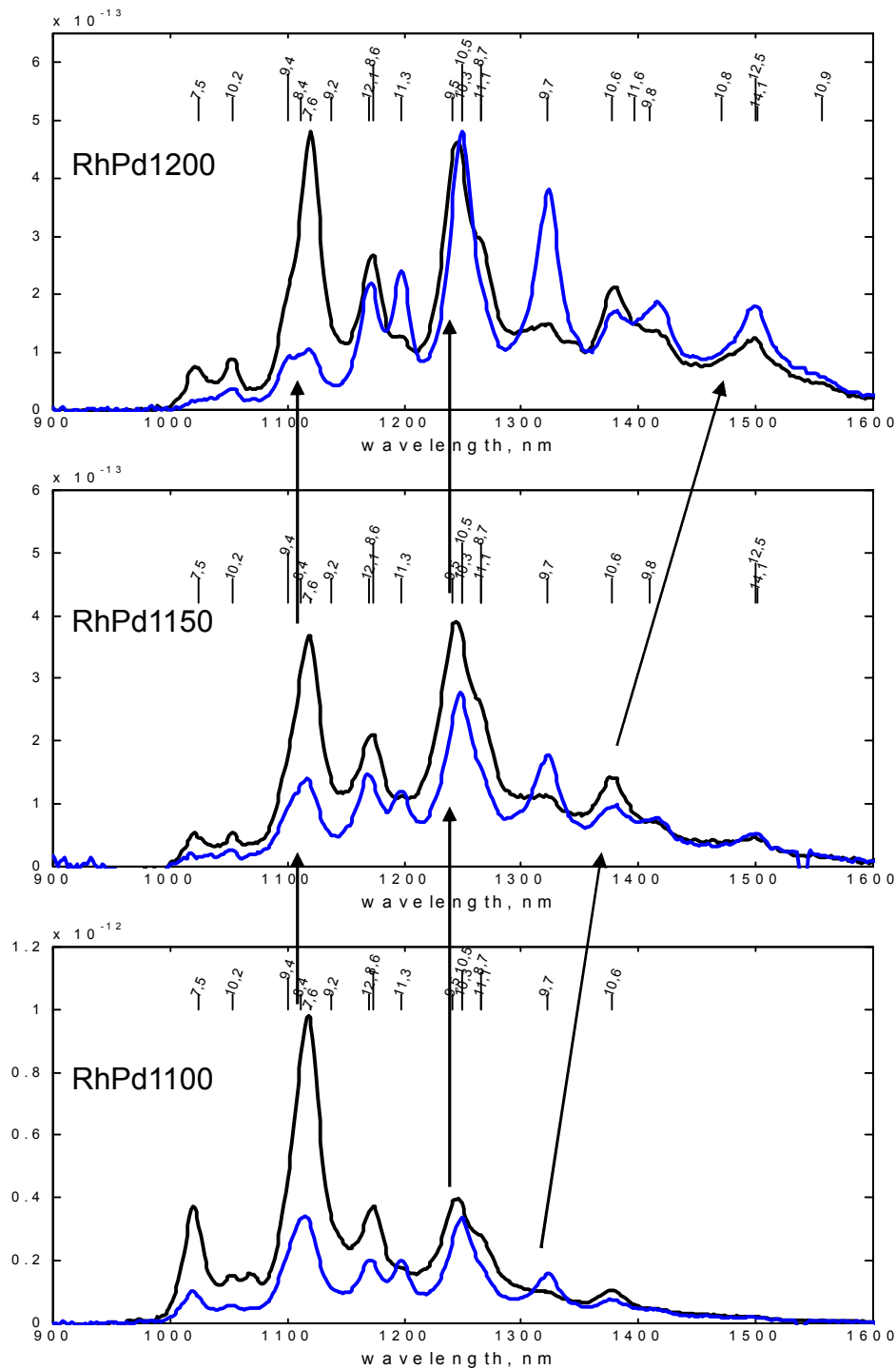
Same exercise for Rh/Pd samples

Absorption spectra.

Temperature increase -> absorption features appear at longer wavelength -> broader diameter distributions



Emission spectra of Rh/Pd samples

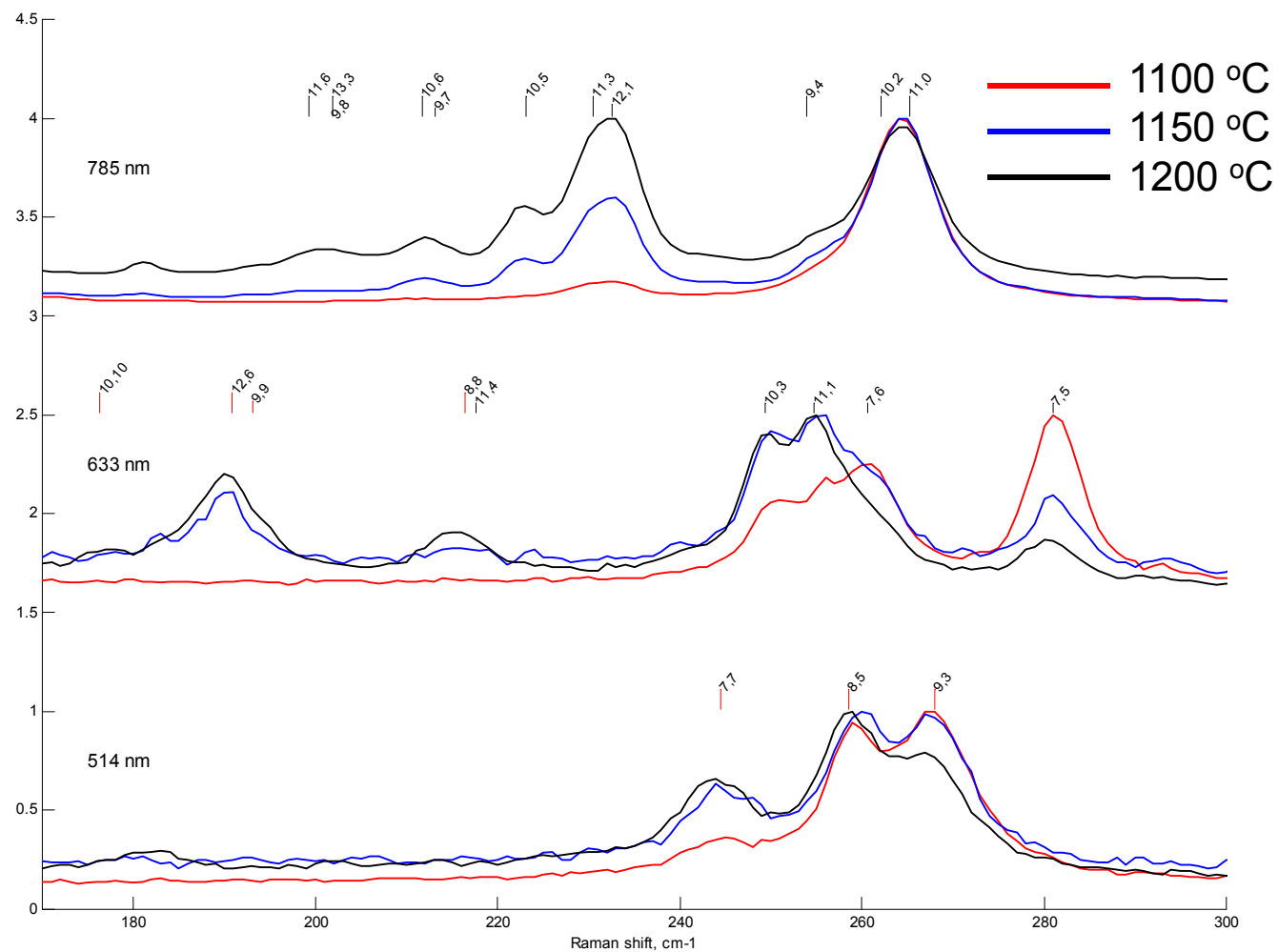


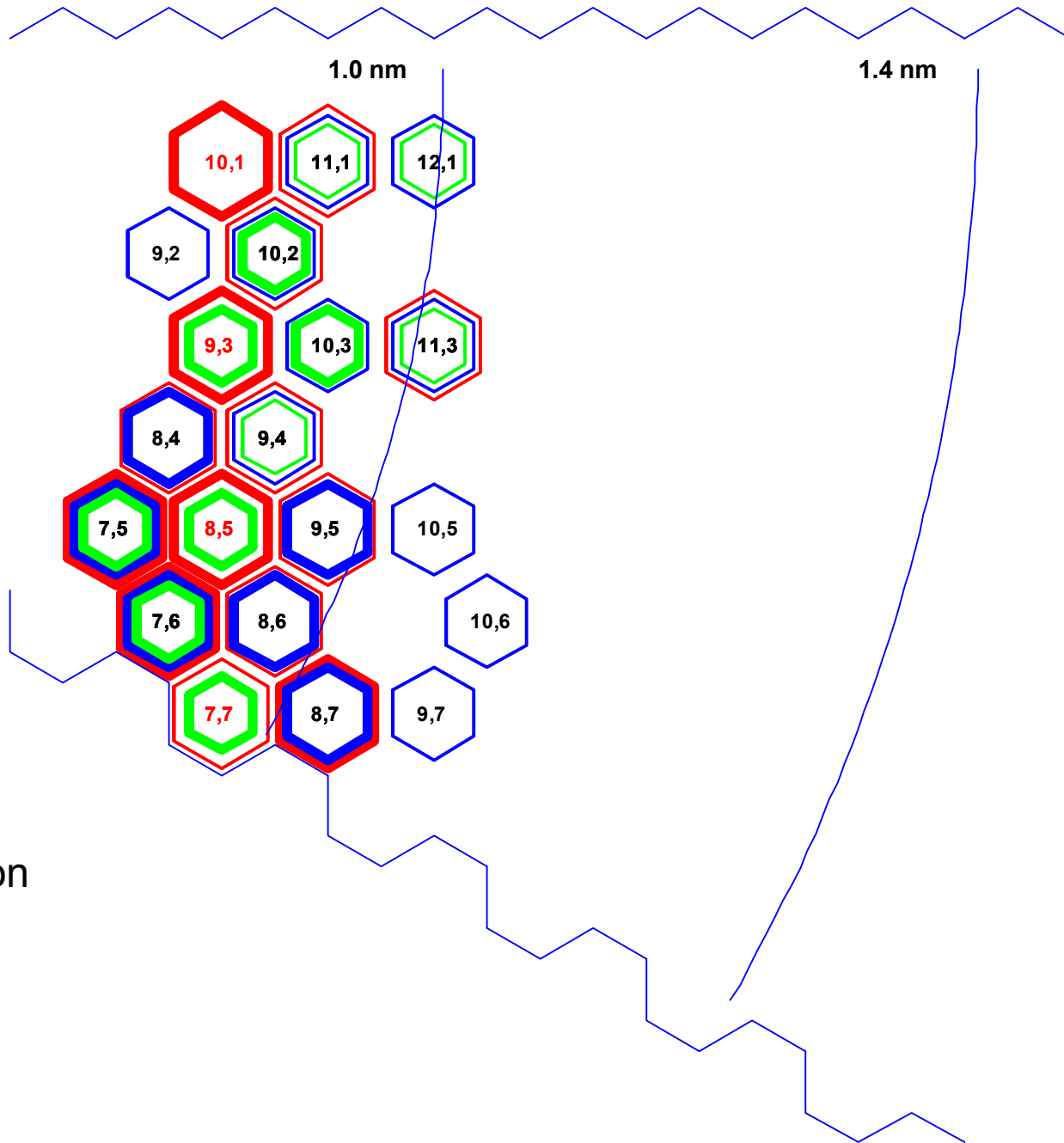
Temperature increase -> emission features shift towards longer wavelength
 -> larger diameter nanotubes
 However, small diameter nanotubes remain on spectra, i.e. diameter distribution is broadened




At 1200 °C, some emission is out of the detector range.

Emission wavelength range is rather broad for 1100°C sample, and gets even broader for 1200 °C sample

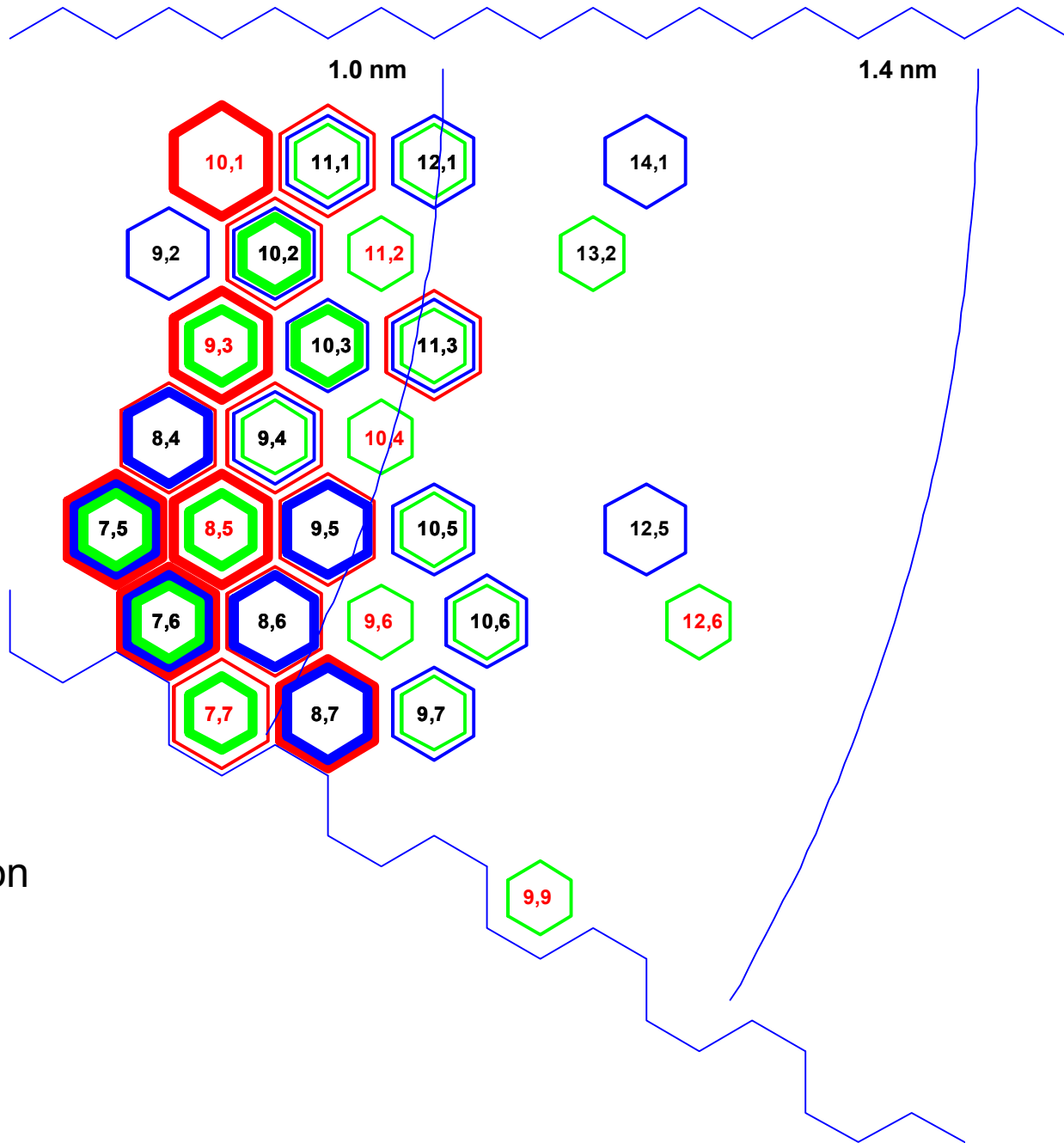
Raman RBM spectra of Rh/Pd samples:



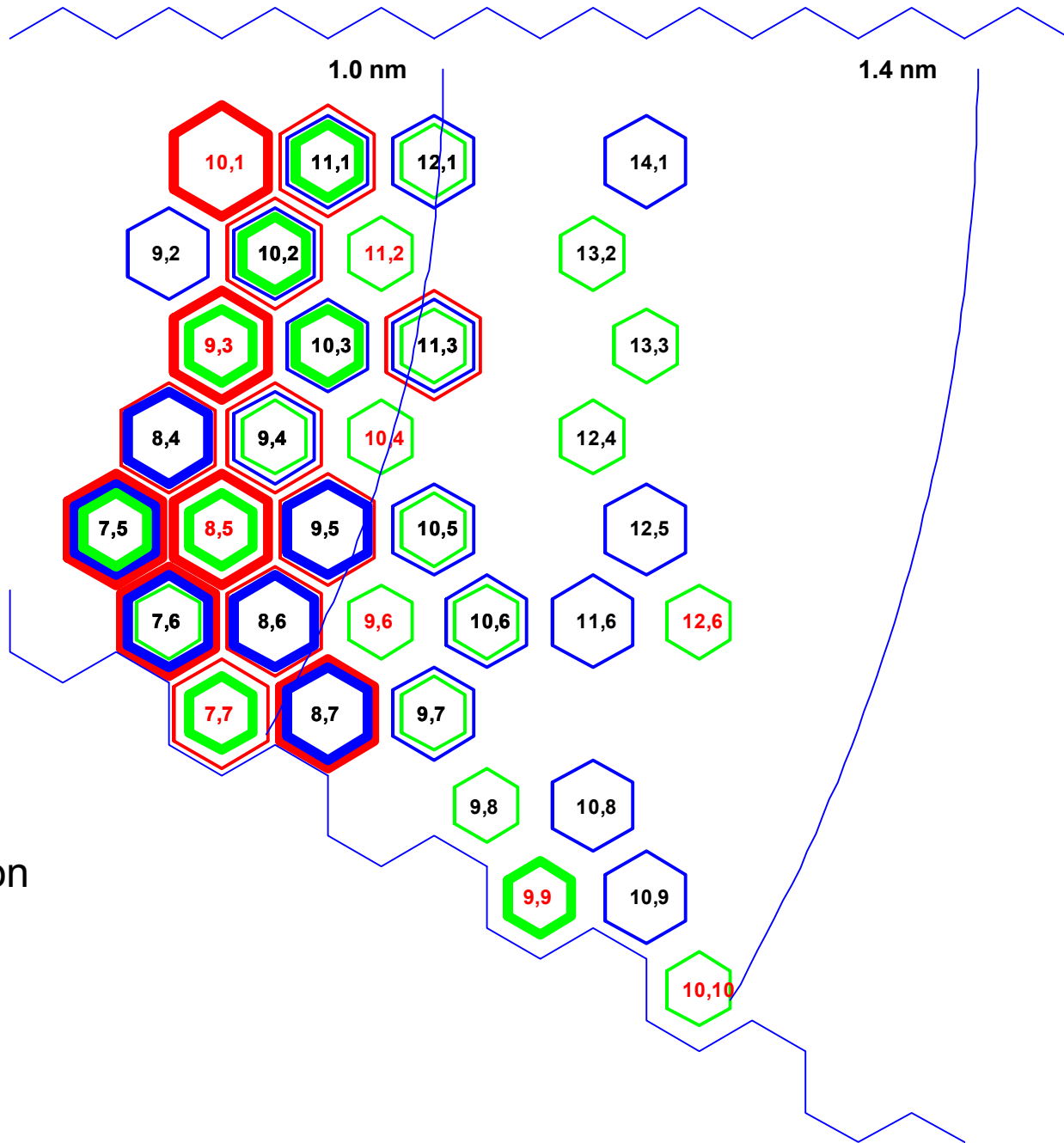


-  Absorption
-  Emission
-  Raman

RhPd1100



RhPd1150



RhPd1200

Observations:

As the temperature is increased:

Average diameter increases

The width of diameter distribution increases. Smallest diameter nanotubes remain

The chiral angle distribution is broader compared to Co/Ni samples. Still somewhat skewed towards 30°

The type distribution is broader compared to Co/Ni samples, and becomes broader at higher temperatures. At the lowest temperature, 1100°C :

Metallic nanotubes:

-armchair metals: (7,7)

-chiral metals: (8,5), (9,3), (10,1)

Semiconductors:

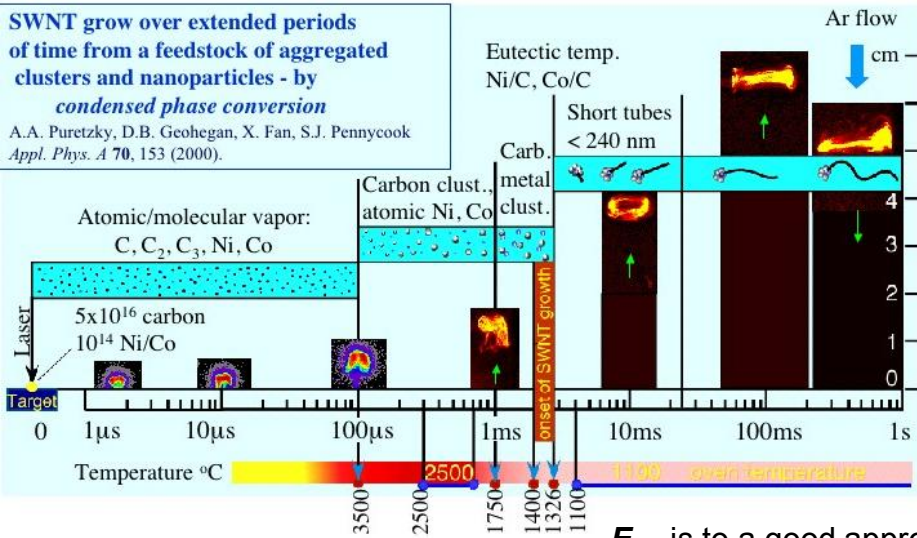
-strongest: (7,6)

-close to arm-chair: (7,5), (8,7)

-less dominant: (8,4), (9,4), (9,5), (10,2), (10,3), (11,1), (11,3), (12,1), (9,7), (10,5), (10,6)

For all Rh/Pd samples, larger diameter nanotubes are associated with larger chiral angles.

Does this observation agree with the nucleation model?



Nanotube nucleation occurs in the 100 μs – 1 ms time frame, from carbon clusters and catalyst vapor.

Lower oven temperature -> faster plume cooling

Rh/Pd -> catalyst atoms attach to carbon clusters earlier

E_c , is to a good approximation independent of tubulet radius (determined by 5 pentagons in a hemisphere).

$E_r = \varepsilon_r L / R$, where ε_r is bending **stiffness of a graphene sheet**, L is length of the cylinder, and R is tubulet radius.

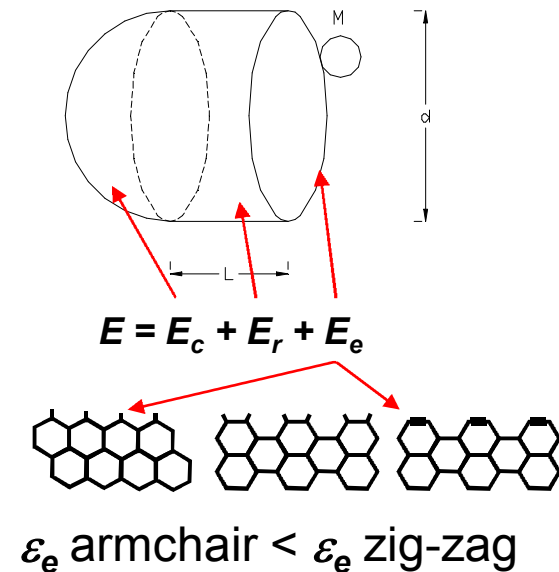
$E_e = 2\pi R \varepsilon_e$, where ε_e is energy of the open edge per unit length.

Minimization of the energy with respect to R for a fixed number of carbon atoms N yields:

$$R \sim (N \varepsilon_r / \varepsilon_e)^{1/3}.$$

Therefore, decrease in the edge energy ε_e will lead to increase in the diameter of a nanotube nucleus.

If ε_e armchair < ε_e zig-zag, nuclei with the edge closest to arm-chair structure will nucleate largest diameter nanotubes.



Conclusions:

- It is possible to produce carbon nanotubes with quite narrow type distribution in PLV setup on Co/Ni catalyst at lower temperature (900 °C), with preference for (8,7) type.
- Type distributions produced with Rh/Pd catalyst are broader, and nanotube yields are lower compared to Co/Ni. The preference for (7,6) type is confirmed.
- Larger diameter nanotubes are associated with larger chiral angles. This agrees with simple energy balance of nanotube nuclei.
- Optical absorption by (8,8) and (9,9) armchair tubes is very small if nonexistent, while optical absorption by (7,7) armchair tube is substantial.
- Authors acknowledge financial support from NASA under contract # NNJ05HI05C and from State of Texas, Space Act Agreement #SAA-AT-07-021 (RAN 0798) (UTA07-099). Authors thank R. Bruce Weisman of Rice University for access to the Nanospectralyzer for photoluminescence measurements.